# The chemistry and mineralogy of the Kinkell tholeiite, Stirlingshire.

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## INTRODUCTION.

THE tholeiite of Kinkell (11 km. north of Glasgow G.P.O.) was described by the first author (Walker, 1930) and an analysis of its residual glass was given in a later publication (Walker, 1935). Since unaltered and separable residual glasses of basaltic rocks are rare, the Kinkell example has been referred to frequently in petrological literature. E. A. Vincent (1950) has made a detailed comparison between the Kinkell glass and a similar one from a tholeiite from Kap Daussy, east Greenland. In view of this and of the important part played by such glasses in discussions on basaltic differentiation, all the major constituents of the Kinkell rock have been isolated and analysed chemically and spectrographically. They are described below together with a fuller account of the field relations of the rock and some comments upon the significance of the new data.

The field work was carried out by the first author (Walker). He is also responsible for writing the article and for the views set forth in it. The separation of the constituent minerals, the determination of their optical properties, and the new chemical analyses are the work of the second author (Vincent), while the third author (Mitchell) estimated the trace elements spectrographically, using the cathode-layer-arc technique (Mitchell, 1940).

## FIELD CHARACTERS.

The Kinkell tholeiite is exposed in an abandoned quarry lying 400 m. WNW. of the eighth milestone from Glasgow on the Glasgow-Lennoxtown road. This quarry is situated on the southerly curving end of a typical E.–W. dike about 20 m. wide. The dike may be traced eastwards by sporadic outcrops and by underground workings to the 'Riggin'

where it forms a multiple intrusion 30 m. wide (Crampton, 1911, pp. 120–121). Material was collected from the exposures in the river south of Milton and from an old quarry immediately south of Antermony Loch. In both cases types were found which, though more altered, closely matched the rock from the southern part of the Kinkell quarry both in fabric and mineralogical composition. Furthermore, these types bear a close resemblance to specimens from other E.–W. tholeiite dikes from the Midland Valley, particularly those of Newton Hill type (Walker, 1935, p. 146). The unusually fresh Kinkell rock may therefore be considered beyond any reasonable doubt to belong to the Permo-Carboniferous quartz-dolerite dike suite of central Scotland.

As stated in the 1930 description (Walker, 1930, pp. 371–372) the type from the northern part of Kinkell quarry differs from the analysed rock from the southern part by being more glassy and containing late skeletal ilmenite in place of chlorophaeite. It is possible that we are dealing here with a multiple intrusion, but the exposures are too scanty to show any line of demarcation between the two types. A decomposed rock was found along the extreme south of the quarry working which appears to represent the chilled basaltic margin of the southern type and has some bearing on its crystallization history.

In the following account only the southern type from Kinkell quarry will be considered, since its mineral constituents permit of relatively easy separation. A new analysis of this type has been used in the present investigation. It is quoted together with the previous analyses in table III.

### MICROSCOPIC CHARACTERS AND CHEMICAL ANALYSES.

A large amount of fresh material was collected in 1947 from the southern part of Kinkell quarry and many new slides prepared from it. These show some features not recorded in 1930 (Walker, 1930, pp. 371–372) when the microscopical examination of the rock was carried out under less favourable conditions.

The mode of the rock was redetermined (Walker) using a Dollar recording micrometer over a total traverse length of 300 mm. with the following result:

Mode (% by weight) of tholeiite from southern part of Kinkell quarry.

| Pyroxene | ... | ... | 27·4 | Chlorophaeite | ... | ... | 4·9 |
| Alagioclase | ... | ... | 26·1 | Apatite | ... | ... | 2·2 |
| Iron ore | ... | ... | 13·0 | OPal | ... | ... | 0·7 |
| Glass | ... | ... | 25·7 | | | | |

The following is an amplification of the 1930 descriptions of the individual mineral constituents.

*Pyroxene.*—About 99 % of the pyroxene consists of pale-brown augite. Most of this forms composite groups with idiomorphic external boundaries but rather irregular internal boundaries. Isolated grains are idiomorphic and there are also large numbers of acicular microlites in the glass with irregular terminations. The relationship of the augite towards the plagioclase is variable and neither mineral can be said to be idiomorphic towards the other. Simple and lamellar twinning on (100) are common and there is some colour zoning. The average grain diameter is 0·3 mm.

TABLE I. Chemical analysis of augite from tholeiite, Kinkell quarry, Stirlingshire. New analysis. (Analyst, H. C. G. Vincent.)

| | Analysis. | Molecular ratios. | | Atomic ratios to 6(O,OH). | | |
|---|---|---|---|---|---|---|
| $SiO_2$ ... | 50·92 | 0·8478 | Si ... | 1·9010 | $\left.\begin{array}{c} \\ 0·099 \end{array}\right\}$ | 2·00 |
| $Al_2O_3$ ... | 2·90 | 0·0285 | Al ... | 0·1276 | $\left\{\begin{array}{c} \\ 0·029 \end{array}\right.$ | |
| $TiO_2$ ... | 1·18 | 0·0148 | Ti ... | 0·0331 | | |
| $Fe_2O_3$ ... | 0·47 | 0·0029 | Fe ... | 0·0132 | | 1·00 |
| FeO ... | 11·11 | 0·1546 | Fe ... | 0·3467 | | |
| MnO ... | 0·33 | 0·0046 | Mn ... | 0·0104 | | |
| | | | | | $\left\{\begin{array}{c} 0·565 \\ \\ 0·305 \end{array}\right.$ | |
| MgO ... | 15·63 | 0·3882 | Mg ... | 0·8702 | | |
| CaO | 17·28 | 0·3081 | Ca ... | 0·6907 | $\left.\begin{array}{c} \\ 0·695 \end{array}\right\}$ | 1·00 |
| $Na_2O$ ... | 0·12 | 0·0019 | Na ... | 0·0042 | | |
| $K_2O$ ... | 0·12 | | | | | |
| $H_2O+$ ... | 0·07 | | $Ca_{35·76}Mg_{45·06}Fe_{19·17}$ | | | |
| $H_2O-$ ... | nil | | Sp. gr. 20° 3·375–3·391 | | | |
| | 100.13 | | 2V 42–50°, $\beta$ 1·696–1·700, $\gamma$:$c$ 42–44°. | | | |

The optical properties given in 1935 (Walker, 1935, p. 141) were confirmed ($\alpha$ 1·699, $\beta$ 1·708, $\gamma$ 1·720, 2V 48°), but are now thought to represent the iron-rich end of the range of composition. $\gamma$ and $\alpha$ were then determined on cleavage flakes and $\beta$ calculated. The highest values were taken and these were probably measured on microlites which would have a preferential tendency to lie in the required direction and would represent the last and most iron-rich stages of pyroxene crystallization.

A very careful redetermination of $\beta$ was made using sodium-light and grains giving centred optic axial interference figures. The range of values obtained was 1·696–1·700, the mean figure being 1·698. The

refractive index of the liquid was checked on a Leitz-Jelley refracto-meter then calibrated against an Abbe refractometer which had been standardized by its reference plate. 2V and $\gamma:c$ were measured on the universal stage on about forty grains, giving a range of values between 42° and 50° with a mean value of 47° for 2V and of 42–44° for $\gamma:c$ (mean 43°). A determination of $\gamma$ on cleavage flakes gave a range of 1·710–1·720.

In addition to the augite there is a small amount of pigeonite (2V 0–14°) as grains which are almost indistinguishable from the main py-roxene. Professor H. H. Hess, who very kindly examined our slides and who first detected the mineral, put the proportion at 6 %, basing it on the shortfall of the calcium atom ratio below the anticipated value (35·76 % against 38 %) using his curves (Hess, 1949, plate I). Many more sections and grains have since been examined by the first two authors and they consider that 6 % is an overestimate. Of over 200 suitably orientated grains examined only one showed a value within the pigeonite range. The proportion of pigeonite in the total pyroxene is probably under 1 % and the pyroxene analysis has therefore been given uncorrected. It is impracticable to separate the two pyroxenes mechanically owing to their close optical resemblance and their specific gravity overlap.

The composition of the augite expressed as atomic ratios is $Ca_{36}Mg_{45}Fe_{19}$ according to the chemical analysis. Using the curves of Hess (1949, plate I) and Muir (1951, fig. 4) the atomic ratios are respectively $Ca_{38}Mg_{38}Fe_{24}$ and $Ca_{39}Mg_{37}Fe_{24}$. No explanation has yet been found for these discrepancies.

*Plagioclase* is the most abundant constituent in the rock by volume, being slightly in excess of both pyroxene and glass. It forms idiomorphic tables with Carlsbad, albite, and occasional pericline twinning. There is no trace of alteration and the crystals show only slight zoning confined to the margins. The bulk of the mineral consists of labradorite $An_{50-58}$ with $\beta$ 1·560, but the extreme margins are more sodic. All of the mineral has a refractive index well above that of Canada balsam and this also applies to the microlitic outgrowths from the terminations. The range of composition, based on specific gravity measurements, is $An_{44-57}$ and the average composition calculated from the analysis (table II) is $Ab_{41\cdot3}An_{55\cdot7}Or_{2\cdot8}Cn_{0\cdot2}$.

The plagioclase is variable in its relations towards the pyroxene, sometimes penetrating it and sometimes being moulded on it. The iron ore, however, is always idiomorphic towards the felspar and is often completely enclosed by it. The absence of true plagioclase microlites

from the glass is noteworthy, but microlitic outgrowths from the terminations of crystals are fairly common.

TABLE II. Chemical analysis of plagioclase from tholeiite, Kinkell quarry, Stirlingshire. New analysis. (Analyst, H. C. G. Vincent.)

| | | | | | | |
|---|---|---|---|---|---|---|
| $SiO_2$ ... | ... 54·50 | $Na_2O$ ... | ... 4·41 | | |
| $TiO_2$ ... | ... 0·12 | $K_2O$ ... | ... 0·47 | | |
| $Al_2O_3$ ... | ... 29·77 | BaO ... | ... 0·07 | Sp. gr. at 22° 2·673–2·692. |
| $Fe_2O_3$* | ... 0·17 | $H_2O$ ... | ... nil | *FeO and $Fe_2O_3$ as $Fe_2O_3$. |
| MgO ... | ... 0·08 | SrO ... | ... n.det. | Composition: |
| CaO ... | ... 10·72 | | | $Ab_{41\cdot3}An_{55\cdot7}Or_{2\cdot8}Cn_{0\cdot2}$. |
| | | | 100·31 | |

*Iron ore* is one of the most conspicuous constituents in the rock and has two distinct habits. The first and dominant type is of early crystallization forming discrete grains and groupings both of which show idiomorphic outlines. They penetrate both plagioclase and augite, some of the smaller individuals being completely enclosed. The second habit is microlitic and skeletal, the mineral being confined to the glass. It is rare in the analysed rock, but is conspicuous in specimens from the north side of the quarry.

The ore was separated by Clerici solution, one hundred grams of the crushed rock yielding 11 gm. of ore. This is lower than the modal percentage of ore (13·0), but iron ore is one of the most variable constituents of the tholeiite. The separated ore was divided by a hand magnet into two fractions with the following properties:

| | (a) Highly magnetic fraction. | (b) Weakly magnetic fraction. |
|---|---|---|
| Weight ... ... | 10·1 gms. | 0·9 gm. |
| Sp. gr. ... ... | 4·25 | 3·56 |
| Ti % ... ... | 10·47 | 25·6 |

These figures suggest that (a) is magnetite with some ilmenite and that (b) is ilmenite with some magnetite, the ratio of (a) to (b) in the rock being approximately 10:1.

Examination of polished sections with vertical illumination confirms the above. Both magnetite and ilmenite are present as separate individuals, the latter in much smaller quantity occurring as rounded grains in the magnetite and also as discrete crystals. Positive identification was given by etch tests: tarnishing and isotropic behaviour for the magnetite; and anisotropism and etch tests for the ilmenite. An X-ray powder photograph of the (b) fraction was identical with a control photograph of undoubted ilmenite from California and contaminating magnetite lines were not discernible.

The tholeiite also contains pyrite as minute spherical grains nearly all

in the oxide iron ore from which they cannot be separated by physical means. They form 0·48 % of the rock by volume or 0·83 % by weight, as measured micrometrically on a polished section viewed by reflected light. This proportion corresponds to a sulphur content of 0·44 %, a figure which shows reasonable agreement with the 0·33 % determined chemically.

*Glass.*—Since the glass in the material collected in 1947 was slightly fresher than that isolated in 1935 another separation was made. The separated material was not, however, reanalysed, although fluorine, boron, and baria were determined and are quoted as additions to the 1935 analyses in table III.

TABLE III. Chemical analyses of tholeiites and their residual glasses.

|  | | 1. | 2. | 3. | 4. | 5. | A. | B. | 6. |
|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | ... | 48·55 | 49·10 | 50·2 | 66·80 | 72·4 | 47·42 | 63·96 | 50·4 |
| $TiO_2$ | ... | 2·94 | 4·02 | 3·0 | 0·18 | 0·2 | 3·98 | 0·78 | 3·2 |
| $Al_2O_3$ | ... | 14·64 | 12·13 | 15·1 | 12·10 | 13·1 | 11·75 | 11·60 | 12·8 |
| $Fe_2O_3$ | ... | 5·42 | 4·61 | 5·6 | 0·97 | 1·1 | 3·39 | 2·93 | 4·9 |
| FeO | ... | 8·28 | 8·92 | 8·5 | 1·50 | 1·6 | 12·79 | 2·76 | 9·4 |
| MnO | ... | 0·23 | 0·15 | 0·2 | n.d. | — | 0·10 | 0·05 | 0·2 |
| MgO | ... | 3·92 | 4·50 | 4·0 | 0·50 | 0·5 | 5·35 | 1·16 | 5·5 |
| CaO | ... | 8·06 | 8·20 | 8·3 | 2·62 | 2·8 | 10·83 | 5·65 | 9·5 |
| BaO | ... | 0·08 | — | 0·1 | 0·29 | 0·3 | — | — | — |
| $Na_2O$ | ... | 2·07 | 2·14 | 2·1 | 2·40 | 2·6 | 2·36 | 1·91 | 2·2 |
| $K_2O$ | ... | 1·51 | 2·10 | 1·6 | 4·20 | 4·6 | 0·55 | 1·55 | 1·2 |
| $H_2O+$ | ... | 2·02 | 2·50 | — | 5·75 | — | 0·95 | 6·12 | — |
| $H_2O-$ | ... | 1·52 | 1·02 | — | 3·00 | — | 0·30 | 0·72 | — |
| S | ... | 0·33 | 0·03 | 0·4 | — | 0·4 | — | — | — |
| $P_2O_5$ | ... | 0·83 | 0·51 | 0·9 | 0·39 | 0·4 | 0·54 | 0·96 | 0·5 |
| $CO_2$ | ... | trace | — | — | — | — | — | — | — |
| $B_2O_3$ | ... | nil | — | — | nil | — | — | — | &c. |
| $ZrO_2$ | ... | nil | — | — | — | — | — | — | |
| F | ... | 0·07 | — | — | 0·01 | — | — | — | 0·2 |
|  | | 100·47 | 99·93 | 100·0 | 100·71 | 100·0 | 100·31 | 100·15 | 100·0 |
|  | | 0·03 | | | | | | | |
|  | | 100·44 | Sp. gr. ... | 2·28–2·31 | — | | 2·99 | 2·43 | — |

1. Tholeiite, dike, Kinkell quarry, Stirlingshire. New analysis. Analyst, H. C. G. Vincent.
2. Tholeiite, dike, Kinkell quarry, Stirlingshire. Analyst, J. Jakob (Walker, 1930, p. 372).
3. Analysis 1, calculated water free.
4. Residual glass from tholeiite of analysis 2. Analysts, W. H. Herdsman (Walker, 1935, p. 150) with new additions by H. C. G. Vincent.
5. Analysis 4 calculated water free.
A. Olivine-tholeiite, dike, Kap Daussy, east Greenland. Analyst, E. A. Vincent (1950, p. 56).
B. Residual glass from tholeiite of analysis A. Analyst, E. A. Vincent (1950, p. 56).
6. Average of 7 analysed Permo-Carboniferous tholeiites from central Scotland, calculated water free.

The glass separated from the 1947 material agrees in its optical properties with that separated previously ($n$ 1·495). It is now evident, however, that the mineral previously regarded as chlorophaeite of late separation is in reality a product of devitrification of the glass. All transitions between this green mineral and unaltered glass are to be
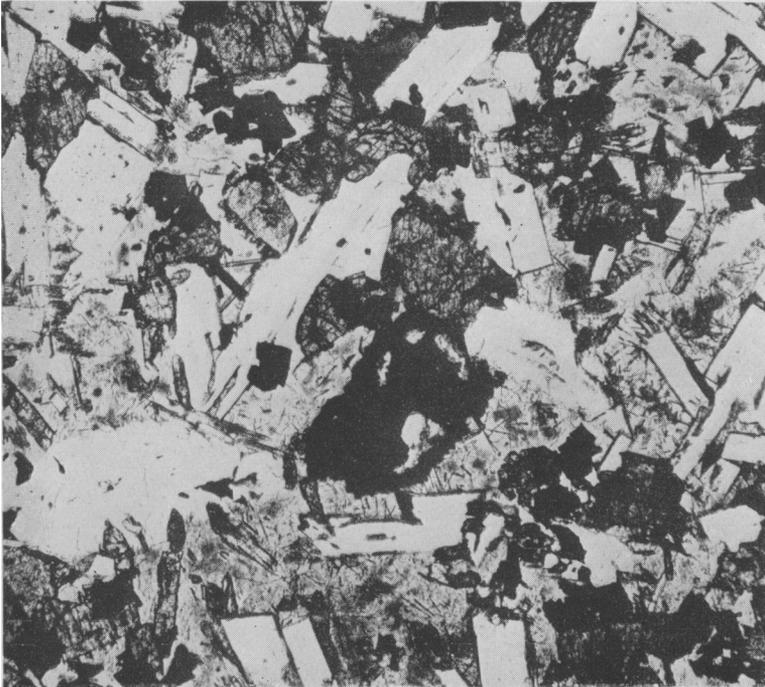


FIG. 1. Photomicrograph of the Kinkell tholeiite, Stirlingshire. A large area of pale glass at the base shows incipient alteration to darker palagonite. Ordinary light × 35.

seen (fig. 1). Except for its isotropic character the green mineral is equivalent to the green chlorite alteration product of the glass from the Kap Daussy tholeiite described by E. A. Vincent (1950, p. 49). It is frequently associated with a little opal.

The glass contains numerous microlites, small idiomorphic prisms of augite, and conspicuous needles of apatite. Inclusions of iron ore and plagioclase are much rarer.

*Apatite*, as in so many rocks belonging to this suite, is an abundant accessory. The idiomorphic needles are commonest in the glass, but

they frequently penetrate the plagioclase and more rarely the augite. A parallel grouping of needles sometimes occurs and the maximum crystal size recorded was 1·1 by 0·06 mm.

*Analyses of Tholeiite.*—The new analysis of the Kinkell tholeiite (no. 1, table III) differs from the previous one (no. 2, table III) in its higher alumina and lower titania and potash. Otherwise the analyses show good agreement. Analysis 1 when calculated water free agrees well with that of the average Permo-Carboniferous tholeiite of Scotland apart from the higher alumina of the Kinkell rock.

## TRACE ELEMENTS IN MINERALS.

The minor elements in the mineral constituents of the tholeiite are given in table IV in order of ionic radius.

TABLE IV. Trace elements in tholeiite constituents as parts per million (analyst, R. L. Mitchell) and comparative data.

| Elements | Ionic radius | Kinkell tholeiite constituents. | | | | Comparisons with Kinkell glass. | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Plagioclase | Augite | Iron ore | Glass | Palisades vein (Walker, 1940) | Skaergaard acid (Wager and Mitchell, 1951) | Caledonian acid (Nockolds and Mitchell, 1948) | Average acid (Tröger, 1935) |
| $V^{+4}$ | 0·61 Å. | — | 200 | 1000 | 5 | 25 | 9 | 80 | — |
| $Ga^{+3}$ | 0·62 | 40 | 10 | 20 | 20 | 50 | 33 | 40 | 15 |
| $Cr^{+3}$ | 0·64 | — | — | — | 10 | 14 | 11 | 60 | 3 |
| $Mo^{+4}$ | 0·68 | — | 2 | 5 | 2 | — | — | — | — |
| $Sn^{+4}$ | 0·74 | — | — | — | — | — | — | — | — |
| $Li^{+1}$ | 0·78 | 2 | 2 | 5 | 1 | — | 20 | 20 | 150 |
| $Ni^{+2}$ | 0·78 | — | 20 | 30 | 5 | 50 | 9 | 20 | 3 |
| $Co^{+2}$ | 0·82 | — | 80 | 150 | — | 250 | 5 | 15 | 10 |
| $Cu^{+2}$ | 0·83 | <10 | <10 | 80 | <10 | 40 | 200 | — | 16 |
| $Sc^{+3}$ | 0·83 | — | 30 | — | — | 1½ | 10 | 10 | 1½ |
| $Zr^{+4}$ | 0·87 | 50 | 30 | — | >1000 | — | 1200 | 200 | 300 |
| $Mn^{+2}$ | 0·91 | 100 | 2500 | 5000 | 150 | — | 800 | 350 | 1000 |
| $Yt^{+3}$ | 1·06 | — | — | — | 30 | — | — | — | — |
| $La^{+3}$ | 1·22 | — | — | — | 30 | — | — | — | — |
| $Sr^{+2}$ | 1·27 | 1200 | 10 | 10 | 2000 | 50 | 450 | 1300 | 90 |
| $Pb^{+2}$ | 1·32 | — | — | — | — | 12 | — | — | — |
| $Ba^{+2}$ | 1·43 | 300 | — | 10 | 3000 | 30 | 1100 | 1300 | 450 |
| $Rb^{+1}$ | 1·49 | — | — | — | 300 | — | — | — | — |

*Vanadium* shows its greatest concentration in the titaniferous iron ore whose $V^{+4}$ (0·61 Å.) is camouflaged by replacing $Ti^{+4}$ (0·64 Å.) in the crystal lattice or is captured in place of $Fe^{+3}$ (0·61). This is in accor-

dance with expectation, for the high proportion of vanadium in titani-
ferous iron ores has often been recorded. A lesser replacement of the
same elements and possibly of $Al^{+3}$ (0·57 Å.) occurs in the pyroxene, but
the element is absent from the plagioclase and insignificant in the glass.

*Gallium* shows no marked concentration in any constituent. The
highest proportion is in the plagioclase where $Ga^{+3}$ (0·62 Å.) probably
replaces $Al^{+3}$ (0·57 Å.) diadochically. It should be noted, however,
that the amount of gallium is somewhat greater than might be expected
in a plagioclase of composition $An_{56}$. Goldschmidt and Peters (1931)
record only 3·7 p.p.m. in bytownite, while Nockolds and Mitchell (1948,
pp. 547–551) found about 40 p.p.m. of gallium in plagioclases within the
andesine range. The amounts in the pyroxene, iron ores, and glass are
normal.

The absence of *chromium* in the three minerals and its small propor-
tion in the glass are noteworthy, for the average value for basic rocks is
of the order of 300–400 p.p.m. Probably the element entered the early
crystallates easily during pre-injection differentiation, took no part in
the middle stages of crystallization, and thus showed a minor concentra-
tion in the residual liquid as represented by the glass.

*Molybdenum* occurs in very small proportions showing a concentra-
tion in the iron ore. It is possible that it is confined here to the pyrite
in view of its marked affinity for sulphur. *Tin* is absent from all consti-
tuents.

The proportion of *lithium* is also very small throughout. Its concentra-
tion in the iron ore is perhaps due to the presence of magnesium, both
elements having the same ionic radius (0·78 Å.).

The distribution of *nickel* and *cobalt* between the mineral constituents
is similar. The latter occurs in greater amount, but both show maximum
concentration in the iron ore with lesser proportions in the pyroxene.
$Ni^{+2}$ (0·78 Å.) probably replaces $Mg^{+2}$ (0·78 Å.) in the pyroxene, but the
position of $Co^{+2}$ (0·82 Å.) is doubtful though it possibly substitutes for
$Fe^{+2}$ (0·83). It is possible that both nickel and cobalt occur in the
pyrite of the rock. The association of cobalt with the pyrite of the
Triassic quartz-diabases of Pennsylvania is well marked (A. F. Budding-
ton, personal communication).

The marked concentration of *copper* in the iron ore is again most
probably in the pyrite (Wager and Mitchell, 1951, p. 190), the substitu-
tion of $Cu^{+2}$ (0·83 Å.) for $Fe^{+2}$ (0·83) in oxides being relatively unimpor-
tant. Elsewhere the proportion of copper is insignificant and below the
average for that element.

*Scandium* is confined to the pyroxene where $Sc^{+3}$ (0·83 Å.) occupies the $Fe^{+2}$ (0·83 Å.), $Mg^{+2}$ (0·78 Å.), or $Ca^{+2}$ (1·06 Å.) positions in the structure. The distribution and proportion of the element are normal.

The small amount of *zirconium* in the plagioclase and pyroxene is probably in zircon which, however, was not recorded microscopically. The marked concentration of this element in the silicic residual glass is normal.

The proportion of *manganese* in the rock (0·23 % MnO) is normal and there is a marked concentration of the element in the pyroxene and iron ore where $Mn^{+2}$ (0·91 Å.) replaces $Fe^{+2}$ (0·83 Å.) diadochically. The proportion in the acid residual glass is lower than the average for granites (500 p.p.m.) and the relatively small amount in the plagioclase doubtless represents minute inclusions of inseparable iron ore rather than diadochic replacement of $Ca^{+2}$ (1·06 Å.) in the felspar structure.

*Thallium* was recorded in both the plagioclase and the glass, but since Clerici solution was used in the separation process, the results are rendered suspect by the possibility of contamination and are therefore omitted.

*Yttrium* and *lanthanum* are restricted to the residual glass of the tholeiite which is in accordance with expectation. Their relatively large ionic radius (1·05Å. and 1·06 Å.) prevent substitution for ferrous iron and magnesium in the dark minerals. The amount in the glass is normal.

The distribution of *strontium* and *barium* in the tholeiite is similar, both showing moderate concentration in the plagioclase and a greater concentration (particularly in the case of barium) in the residual glass. This distribution is normal though the proportion of both elements in the tholeiite is above the average and the values may be a little too high. Both $Ba^{+2}$ (1·43 Å.) and $Sr^{+2}$ (1·27 Å.) substitute for $K^{+1}$ (1·33 Å.) in the potash-felspar structure most of which is contained potentially in the residual glass. The lower proportion of barium in the plagioclase structure, where $Ba^{+2}$ (1·43 Å.) and $Sr^{+2}$ (1·27 Å.) are camouflaged replacing $Ca^{+2}$ (1·06) diadochically, is due to the high ionic radius of barium. The lower ionic radius of strontium promotes its incorporation.

*Lead* is absent from all constituents of the tholeiite.

*Rubidium*, like barium, is enriched in the residual glass, owing to its high ionic radius (1·49 Å.), and the proportion is normal. It is camouflaged on crystallization in the potash-felspar structure.

*General Comments.*—The crystalline constituents of the tholeiite

belong to what may be termed the main stage of crystallization. The occurrence of about 30 % of glass in the rock gives a clear-cut natural break between the main stage and what potentially would be the later stages. The chemical composition of the pyroxene, as well as the absence of chromium, indicate that the earliest crystallates do not enter into the mineral composition of the rock which, as will be shown below, is slightly advanced along the liquid line of descent from saturated basalt magma. This is also in keeping with the distribution of the minor elements in the rock, there being very few anomalies.

## CRYSTALLIZATION HISTORY OF KINKELL THOLEIITE.

In his illuminating comparative study of the Kap Daussy and Kinkell tholeiites E. A. Vincent (1950) has shown clearly the variation of the main oxides in the chemical analyses and has given a picture of the differentiation trend. The additional data, now presented, allow this picture to be modified in certain respects though the broad outline remains unchanged.

It has been shown above that the minor elements of the Kinkell tholeiite behave as expected, entering into the crystal structures or being concentrated in the residual glass according to their ionic radius and electrostatic charge. The picture is thus filled in in detail.

Turning to the major constituents Vincent (1950, p. 59) has illustrated the crystallization trends of the two tholeiites and of calc-alkali magma in general by means of the triangular diagram originated by Wager and Deer (1939) with FeO, MgO, and $K_2O+Na_2O$ as co-ordinates. This diagram serves well for intrusions, such as the Skaergaard pluton and the Palisade diabase sill, which are low in $Fe_2O_3$, but when, as in the Kinkell and Kap Daussy tholeiites, the proportion of ferric oxide is much higher the diagram should be modified to include $Fe_2O_3$ with FeO. This has been done with good effect by Tilley (1950, pp. 52–53) and by H. R. Cornwall (1951, pp. 165–169). The use of molecular proportions (Walker 1952) is a further improvement, though it is doubtful whether the additional time involved in calculation is justified in practice.

The diagram used in fig. 2 has weight percentages of $FeO+Fe_2O_3$, MgO, and $Na_2O+K_2O$ as co-ordinates. It shows all the available superior analyses of the late Palaeozoic tholeiite province of Scotland and northern England to which the Kinkell tholeiite belongs. Included amongst these are five new analyses of a differentiated quartz-dolerite sill from Northfield, Stirlingshire (Walker, 1952). Analyses of the

Kap Daussy tholeiite and glass, and of the average rhyolite, dacite, andesite, and basalt of Daly (1933, pp. 9–17) are quoted for comparison, and the new analysis of the Kinkell tholeiite is joined to that of the residual glass by a tie-line.
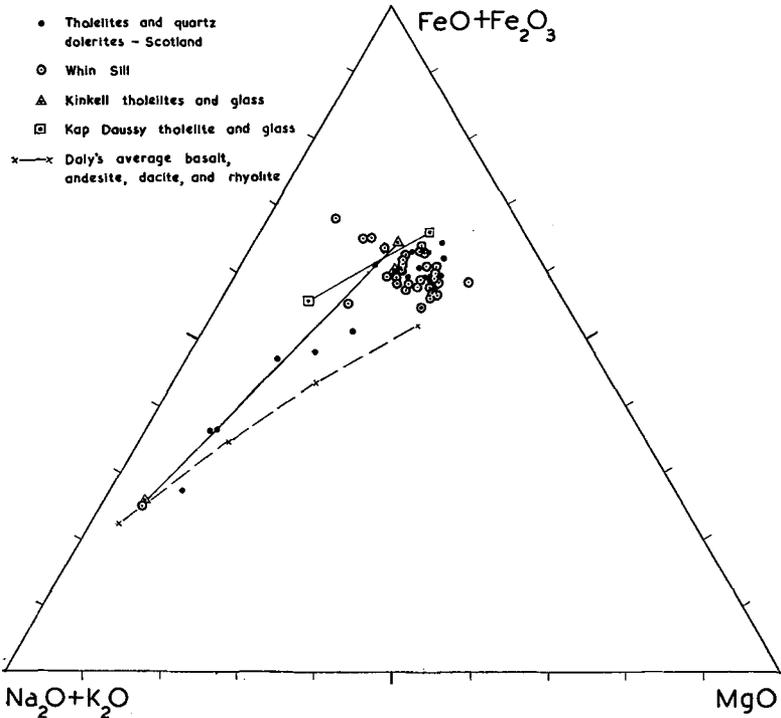


FIG. 2. Crystallization trends of tholeiites.

The two points representing the analyses of the Kinkell tholeiite lie within a closely spaced group of points plotted from analyses of undifferentiated types of the same suite from Scotland and northern England. The chemical composition of the Kinkell tholeiite is thus normal. Furthermore, the tie-lines between either Kinkell tholeiite analyses and that of the residual glass lie just along the line of variation for the suite, proving thereby that the crystallization sequence in the Kinkell rock was again normal.

The corresponding tie-line for the Kap Daussy analyses lies parallel to but slightly above the line of variation for the British suite, as might

be expected in view of the higher degree of fractionation and iron enrichment in the Greenland province.

The variation trend of the British suite lies very close though slightly above the line joining Daly's averages for rhyolite, dacite, andesite, and basalt (Daly, 1933, pp. 9–17) which represents normal calc-alkali variation. Thus the diagram with total iron as the upper co-ordinate brings out the normal character of tholeiitic differentiation, whereas, if $Fe_2O_3$ is omitted for that co-ordinate, the trend-lines in question show considerable separation (Walker and Poldervaart, 1949, p. 659).

The decomposed chill phase of the Kinkell tholeiite shows 8–10 % of phyric plagioclase and augite plainly recognizable by their habit. The two minerals occur in almost equal proportions by volume and it is therefore clear that, when the tholeiite was injected, both constituents had started to crystallize and formed together under 10 % of solid phase. The normal tholeiite represents a stage where the solid phase had increased to about 70 % and here too the plagioclase and pyroxene occur in roughly equal proportions. Evidently the two minerals had the same crystallization range and maintained approximately equal rates of crystallization up to a fairly late stage—a point of some importance. Primary iron ore could not be recognized with any certainty in the decomposed chill phase and thus its crystallization range could not be estimated. It seems, however, to be a fairly early mineral, the crystallization of which tends to build up silica in the residual liquid.

*Summary.*—The unaltered tholeiite of Kinkell quarry, Stirlingshire, has been reinvestigated and the mineral constituents have been separated and analysed both chemically and spectrographically. No anomalies were found and the distribution of the trace elements in the rock is normal. The two main mineral constituents of the rock—augite and labradorite—had the same crystallization ranges and maintained approximately equal rates of crystallization until the rock was 70 % crystalline.

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